

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

A.N. Speca

BEFORE THE EXAMINER:

Unassigned

Group Art Unit No.:

Unassigned

Serial No.: Unassigned

Divisional of U.S.S.N. 09/339,128

Filed: Herewith

Attorney Docket No.: 98B045/5

For: Highly Active Supported
Catalyst Compositions

Baytown, Texas

February 11, 2002

BOX PATENT APPLICATION

Commissioner for Patents
Washington, D.C. 20231

Sir:

Applicants respectfully request entry of the following amendments prior to the examination of the Divisional Application filed herewith.

IN THE SPECIFICATION

Please replace the phrase on page 1 after the title, "This is a Regular Application based on a Provisional Application No. 60/098007 filed on August 26, 1998" with the following statement:

--CROSS-REFERENCE TO RELATED APPLICATION

The present application is a Divisional application of, and claims priority to, U.S.S.N. 09/339,128, filed on June 24, 1999, which claims priority to Provisional Patent Application U.S.S.N. 60/098,007.--

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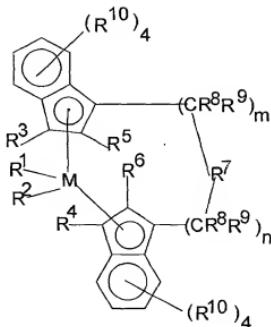
IN THE CLAIMS

Please cancel Claims 1-22. Please add new 23-52:

23. (new) An olefin polymerization method comprising the steps of contacting a polymerizable olefin with a supported catalyst composition comprising one or more fluorided support compositions; one or more metallocenes; and one or more activators, characterised in that the degree of fluoridation of the support allows association between the fluorided support and one or more activators such that when contacted with one or more metallocenes and α -olefin monomers, the supported catalyst composition exhibits a productivity of from 919 to 6012 g polymer/g metallocene-hr.
24. (new) The method of Claim 23, wherein the activity of the composition is from 38.8 to 207.3 kg polymer/mM metallocene-hr.
25. (new) The method of Claim 23, the support having a fluorine concentration is in the range of from 0.01 to 10.0 millimoles of fluorine per gram of support.
26. (new) The method of Claim 23, the support having a fluorine concentration is in the range of from 0.6 to 3.5 wt% of the support.
27. (new) The method of Claim 23, wherein the one or more activators are selected from alkylalumoxanes (MAO), non-coordinating anions, and activator anion neutral precursors, and combinations thereof.
28. (new) The method of Claim 23, wherein the one or more activators is selected from highly fluorinated tri-arylborane compounds and mixtures thereof.

29. (new) The method of Claim 23, wherein the activator is selected from trisperfluorophenyl borane, trisperfluoronaphthyl borane, trisperfluorobiphenyl borane, tris(3,5-di(trifluoromethyl)phenyl)borane, tris(di-t-butylmethylsilyl)perfluorophenylborane, and mixtures thereof.

30. (new) The method of Claim 23, wherein the one or more metallocenes is represented by the following:

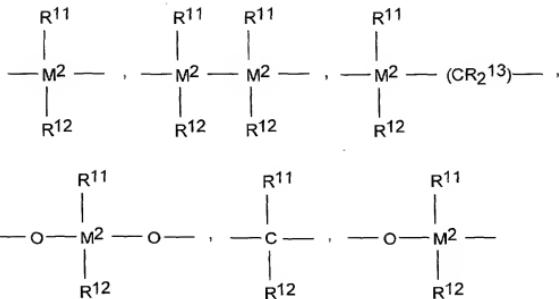


wherein M is a metal of Group 4, 5, or 6 of the Periodic Table;

R¹ and R² are identical or different, and are one of a hydrogen atom, a C₁-C₁₀ alkyl group, a C₁-C₁₀ alkoxy group, a C₆-C₁₀ aryl group, a C₆-C₁₀ aryloxy group, a C₂-C₁₀ alkenyl group, a C₇-C₄₀ arylalkyl group, a C₇-C₄₀ alkylaryl group, a C₈-C₄₀ arylalkenyl group, or a halogen atom;

R⁵ and R⁶ are identical or different, are one of a halogen atom, a C₁-C₁₀ alkyl group, which may be halogenated, a C₆-C₁₀ aryl group, which may be halogenated, a C₂-C₁₀ alkenyl group, a C₇-C₄₀ -arylalkyl group, a C₇-C₄₀ alkylaryl group, a C₈-C₄₀ arylalkenyl group, a -NR₂¹⁵, -SR¹⁵, -OR¹⁵, -OSiR₃¹⁵ or -PR₂¹⁵ radical, wherein R¹⁵ is one of a halogen atom, a C₁-C₁₀ alkyl group, or a C₆-C₁₀ aryl group;

R⁷ is



-B(R¹¹)-, -Al(R¹¹)-, -Ge-, -Sn-, -O-, -S-, -SO-, -SO₂-, -N(R¹¹)-, -CO-, -P(R¹¹)-, or -P(O)(R¹¹);

wherein R¹¹, R¹² and R¹³ are identical or different and are a hydrogen atom, a halogen atom, a C₁-C₂₀ alkyl group, a C₁-C₂₀ fluoroalkyl group, a C₆-C₃₀ aryl group, a C₆-C₃₀ fluoroaryl group, a C₁-C₂₀ alkoxy group, a C₂-C₂₀ alkenyl group, a C₇-C₄₀ arylalkyl group, a C₈-C₄₀ arylalkenyl group, or a C₇-C₄₀ alkylaryl group; and wherein R¹¹ and R¹², or R¹¹ and R¹³, together with the atoms binding them, can form ring systems;

M² is silicon, germanium or tin;

R⁸ and R⁹ are identical or different and have the meanings stated for R¹¹;

m and n are identical or different and are zero, 1 or 2, m plus n being zero, 1 or 2; and

the radicals R³, R⁴, and R¹⁰ are identical or different and have the meanings stated for R¹¹, R¹² and R¹³.

31. (new) The method of Claim 23, wherein the one or more metallocenes is selected from Dimethylsilanediylbis (2-methyl-4-phenyl-1-indenyl) zirconium dimethyl; Dimethylsilanediylbis(2-methyl-4,5-benzoindenyl) zirconium dimethyl; Dimethylsilanediylbis(2-methyl-4,6-diisopropylindenyl) zirconium dimethyl; Dimethylsilanediylbis(2-ethyl-4-

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phenyl-1-indenyl) zirconium dimethyl; Dimethylsilandiylbis (2-ethyl-4-naphthyl-1-indenyl) zirconium dimethyl; Dimethylsilandiylbis(2-methyl-4-(1-naphthyl)-1-indenyl) zirconium dimethyl; Dimethylsilandiylbis(2-methyl-4-(2-naphthyl)-1-indenyl) zirconium dimethyl; Dimethylsilandiylbis(2-methyl-indenyl) zirconium dimethyl; Dimethylsilandiylbis(2-methyl-4,5-diisopropyl-1-indenyl) zirconium dimethyl; Dimethylsilandiylbis(2,4,6-trimethyl-1-indenyl) zirconium dimethyl; Dimethylsilandiylbis(2-methyl-1-indenyl) zirconium dimethyl; Dimethylsilandiylbis(2-ethyl-1-indenyl) zirconium dimethyl; Dimethylsilandiylbis(2,5,6-trimethyl-1-indenyl) zirconium dimethyl; Dimethylsilandiylbis (2-methyl-4-phenyl-1-indenyl) zirconium dichloride; Dimethylsilandiylbis(2-methyl-4,5-benzoindenyl) zirconium dichloride; Dimethylsilandiylbis(2-methyl-4,6-diisopropylindenyl) zirconium dichloride; Dimethylsilandiylbis(2-ethyl-4-phenyl-1-indenyl) zirconium dichloride; Dimethylsilandiylbis (2-ethyl-4-naphthyl-1-indenyl) zirconium dichloride; Dimethylsilandiylbis(2-methyl-4-(1-naphthyl)-1-indenyl) zirconium dichloride; Dimethylsilandiylbis(2-methyl-4-(2-naphthyl)-1-indenyl) zirconium dichloride; Dimethylsilandiylbis(2-methyl-indenyl) zirconium dichloride; Dimethylsilandiylbis(2-methyl-4,5-diisopropyl-1-indenyl) zirconium dichloride; Dimethylsilandiylbis(2,4,6-trimethyl-1-indenyl) zirconium dichloride; Dimethylsilandiylbis(2-ethyl-1-indenyl) zirconium dichloride, and Dimethylsilandiylbis(2,5,6-trimethyl-1-indenyl) zirconium dichloride, and mixtures thereof.

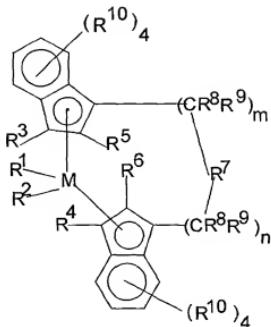
32. (new) The method of Claim 23, wherein the fluorided support composition is selected from the following fluorided supports: talc, clay, silica, alumina, magnesia, zirconia, iron oxides, boria, calcium oxide, zinc oxide, barium oxide thoria, aluminum phosphate gel, polyvinylchloride or substituted polystyrene, and mixtures thereof.

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33. (new) The method of Claim 23, wherein the supported catalyst composition exhibits a productivity of from 919 to 5180 g polymer/g metallocene-hr.
34. (new) The method of Claim 23, wherein the supported catalyst composition exhibits a productivity of from 1125 to 6012 g polymer/g metallocene-hr.
35. (new) The method of Claim 23, wherein the supported catalyst composition exhibits a productivity of from 1125 to 5180 g polymer/g metallocene-hr.
36. (new) The method of Claim 23, wherein the α -olefin monomers are propylene.
37. (new) The method of Claim 23, wherein a support and a fluoriding agent are contacted with one another at from 200°C to 600°C to produce the fluorided support composition.
38. (new) A polyolefin produced by the method of Claim 23.
39. (new) An olefin polymerization method comprising the steps of contacting a polymerizable olefin with a supported catalyst composition comprising a fluorided support composition; and at least one highly fluorinated tris-arylborane bound to the fluorided support composition.
40. (new) The method of Claim 39, wherein the at least one highly fluorinated tris-arylborane is selected from tris-perfluorophenyl borane, trisperfluoronaphthyl borane, trisperfluorobiphenyl borane, tris(3,5-

di(trifluoromethyl)phenyl)borane, tris(di-*t*-butylmethylsilyl)perfluorophenylborane, and mixtures thereof.

41. (new) The method of Claim 39, wherein the support also comprises at least one metallocene represented by the following:

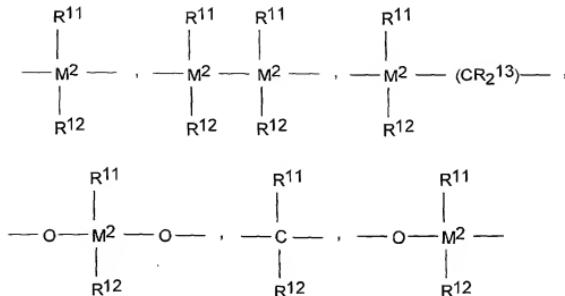


wherein M is titanium, zirconium, or hafnium;

R¹ and R² are identical or different, and are one of a hydrogen atom, a C₁-C₁₀ alkyl group, a C₁-C₁₀ alkoxy group, a C₆-C₁₀ aryl group, a C₆-C₁₀ aryloxy group, a C₂-C₁₀ alk enyl group, a C₇-C₄₀ arylalkyl group, a C₇-C₄₀ alkylaryl group, a C₈-C₄₀ arylalkenyl group, or a halogen atom;

R^5 and R^6 are identical or different, are one of a halogen atom, a C_1 - C_{10} alkyl group, which may be halogenated, a C_6 - C_{10} aryl group, which may be halogenated, a C_2 - C_{10} alkenyl group, a C_7 - C_{40} -arylalkyl group, a C_7 - C_{40} alkylaryl group, a C_8 - C_{40} arylalkenyl group, a $-NR_2^{15}$, $-SR^{15}$, $-OR^{15}$, $-OSiR_3^{15}$ or $-PR_2^{15}$ radical, wherein R^{15} is one of a halogen atom, a C_1 - C_{10} alkyl group, or a C_6 - C_{10} aryl group;

\mathbb{R}^7 is



-B(R¹¹)-, -Al(R¹¹)-, -Ge-, -Sn-, -O-, -S-, -SO-, -SO₂-, -N(R¹¹)-, -CO-,
 -P(R¹¹)-, or -P(O)(R¹¹)-;

wherein R¹¹, R¹² and R¹³ are identical or different and are a hydrogen atom, a halogen atom, a C₁-C₂₀ alkyl group, a C₁-C₂₀ fluoroalkyl group, a C₆-C₃₀ aryl group, a C₆-C₃₀ fluoroaryl group, a C₁-C₂₀ alkoxy group, a C₂-C₂₀ alkenyl group, a C₇-C₄₀ arylalkyl group, a C₈-C₄₀ arylalkenyl group, or a C₇-C₄₀ alkylaryl group; and wherein R¹¹ and R¹², or R¹¹ and R¹³, together with the atoms binding them, can form ring systems;

M² is silicon, germanium or tin;

R⁸ and R⁹ are identical or different and have the meanings stated for R¹¹;

m and n are identical or different and are zero, 1 or 2, m plus n being zero, 1 or 2; and

the radicals R³, R⁴, and R¹⁰ are identical or different and have the meanings stated for R¹¹, R¹² and R¹³.

42. (New) The method of Claim 41, wherein R₁ and R₂ are methyl groups.

43. (new) The method of Claim 39, having a fluorine concentration is in the range of from 0.01 to 10.0 millimoles of fluorine per gram of support.

44. (new) The method of Claim 39, having a fluorine concentration is in the range of from 0.6 to 3.5 wt% of the support.

45. (new) The method of Claim 39, wherein the fluorided support composition is selected from fluorided talc, clay, silica, alumina, magnesia, zirconia, iron oxides, boria, calcium oxide, zinc oxide, barium oxide thoria, aluminum phosphate gel, polyvinylchloride or substituted polystyrene, and mixtures thereof.

46. (new) The method of Claim 39, wherein the support and a fluoriding agent are contacted with one another at from 100°C to 1000°C to produce the fluorided support composition.

47. (new) The method of Claim 39, wherein a support and a fluoriding agent are contacted with one another at from 200°C to 600°C to produce the fluorided support composition.

48. (new) The method of Claim 47, wherein the fluoriding agent is selected from NH₄BF₄, (NH₄)₂SiF₆, NH₄PF₆, NH₄F, (NH₄)₂TaF₇, NH₄NbF₄, (NH₄)₂GeF₆, (NH₄)₂SmF₆, (NH₄)₂TiF₆, (NH₄)₂ZrF₆, MoF₆, ReF₆, GaF₃, SO₂ClF, F₂, SiF₄, SF₆, ClF₃, ClF₅, BrF₅, IF₇, NF₃, HF, BF₃, NHF₂ and NH₄HF₂ and mixtures thereof.

49. (new) The method of Claim 39, wherein the supported catalyst composition exhibits a productivity of from 919 to 5180 g polymer/g metallocene-hr.

50. (new) The method of Claim 39, wherein the supported catalyst composition exhibits a productivity of from 1125 to 6012 g polymer/g metallocene-hr.

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51. (new) The method of Claim 39, wherein the supported catalyst composition exhibits a productivity of from 1125 to 5180 g polymer/g metallocene·hr.
52. (new) A polyolefin produced by the method of Claim 39.

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REMARKS

In the original case of Serial No. 09/339,128, the Examiner restricted claims 14-15, and 18 as a separate group. The Applicant now files this Divisional Application to prosecute those claims. In the present Divisional Application, Claims 1-22 are cancelled, and replaced by new Claim 23-52 in order to overcome rejections on the original Claims 1-13, which are related to the method claims 14-15, 18. The new claims find support throughout the specification as filed, and in particular as highlighted below:

In Claim 23, "A supported catalyst composition comprising one or more fluoridized support compositions; one or more metallocenes; and one or more activators" finds support on page 4, lines 11-13, and throughout the specification.

In Claim 23, "a-olefin monomers" finds support on page 18, lines 29-31, and throughout the specification.

In Claim 23, "a productivity of from 919 to 6012 g polymer/g metallocene-hr" finds support on page 35, Table 6 value in Example 33 and Example 55 of Table 14, page 43, both productivity values calculated from polypropylene polymerization under similar conditions.

In Claim 24, the claimed values also find support in Table 6, Examples 33 and 35, and throughout the specification.

In Claim 25, the claimed values find support on page 6, lines 6-7.

In Claim 26, the claimed values find support on page 6, lines 10-12.

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In Claim 27, the "alkylalumoxanes (MAO), non-coordinating anions, and activator anion neutral precursors, and combinations thereof" are selected from page 14, lines 6-15, page 15 and 16, and page 17, lines 1-15, respectively, and throughout the specification.

Claim 28 finds support from page 17, lines 24-25, and throughout the specification.

Claim 29 finds support from page 17, lines 20-25, and throughout the specification.

Claims 30 and 31 finds support from pages 7-13, and throughout the specification.

Claim 32 finds support on page 5, lines 1-7.

Claim 33 finds support in values from Table 6 on page 35, the propylene polymerizations being carried out under similar conditions.

Claim 34 and 35 find support as above, the value of "1125 g polymer/g catalyst-hr. found on page 36, Table 9 in Example 41, the propylene polymerizations being carried out under similar conditions as the upper limit value.

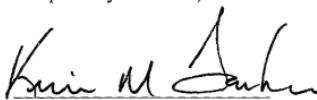
Claims 36 and 38 find support on pages 18-19, and throughout the specification.

Support for the Claims 39-52 are as stated above, and in the previously submitted claims from which this Divisional Application is filed.

The Applicant believes the claims 23-52 to be allowable as submitted, and requests allowance. The Examiner is invited to telephone the undersigned attorney if there are any other issues outstanding which have not been presented to the Examiner's satisfaction.

Respectfully submitted,

February 11/02
Date



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HIGHLY ACTIVE SUPPORTED CATALYST COMPOSITIONS

5 This is a Regular Application based on a Provisional Application No. 60/098007 filed on August 26, 1998.

6 [see page 2 of "Prelim
Amendment"]

FIELD OF INVENTION

10 This invention relates generally to supported catalysts, and more particularly to supported metallocene catalysts and methods for their production and use.

BACKGROUND

15 Metallocene catalyst systems and their use for olefin polymerization are well known. Metallocene catalysts are single-sited and differently activated compared to conventional Ziegler-Natta catalysts. A typical metallocene catalyst system includes a metallocene catalyst, a support, and an activator. Upon attaching or "fixing" the catalyst to the support, the catalyst is generally referred to as a supported catalyst. For many polymerization processes, supported catalysts are required, and various methods for attaching metallocene catalysts to a support are known in the art. Supports suitable for use with metallocene catalyst are generally porous materials and can include organic materials, inorganic materials and inorganic oxides.

20 However, many supports contain reactive functionalities. In some instances, these reactive functionalities may deactivate or reduce the activity of the catalyst fixed to the support. When this occurs, the addition of more catalyst to the catalyst system may be necessary to ensure sufficient polymer production during olefin polymerization. Increasing the catalyst concentration in the catalyst system to compensate for activity reduction caused by reactive functionalities is generally undesirable for many reasons. For instance, generally the addition of more catalyst may also require the addition of more activator. As such, increasing the concentrations of both catalyst and activator to overcome the effects of catalyst

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HIGHLY ACTIVE SUPPORTED CATALYST COMPOSITIONS**CROSS-REFERENCE TO RELATED APPLICATION**

5 The present application is a Divisional application of, and claims priority to, U.S.S.N. 09/339,128, filed on June 24, 1999, which claims priority to Provisional Patent Application U.S.S.N. 60/098,007.

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20 25 30 However, many supports contain reactive functionalities. In some instances, these reactive functionalities may deactivate or reduce the activity of the catalyst fixed to the support. When this occurs, the addition of more catalyst to the catalyst system may be necessary to ensure sufficient polymer production during olefin polymerization. Increasing the catalyst concentration in the catalyst system to compensate for activity reduction caused by reactive functionalities is generally undesirable for many reasons. For instance, generally the addition of more catalyst

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